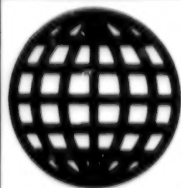


JPRS-UCH-93-001  
22 January 1993



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# ***JPRS Report***

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***Central Eurasia:  
Chemistry***

# Science & Technology

## CENTRAL EURASIA: Chemistry

JPRS-UCH-93-001

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**Analysis of Complex of Parameters of Smoke Aerosols ]**

937M0016A Kiev *FIZIKA AERODISPERSNYKH SISTEM* in Russian No 33, Mar 90 (manuscript received 24 Oct 88) pp 3-8

[Article by A. V. Kolpakov, candidate of mathematical sciences S. V. Lopatenko, scientific associate V. A. Salov, junior scientific associate Ye. I. Titov, Odessa University; UDC 551.510.42:551.588.7]

[Abstract] Measurement of parameters of smoke systems arising during pyrolysis of 10 substances (wood, rubber, polyethylene, foam plastic, vinyl polychloride, cotton fabric, wool, process oil, oil-base paint and nitrocellulose enamel) showed that measurements of smoke particles by a nephelometer and a VDK counter will correspond to one another if you take into account the light-absorbing and light-scattering capacities of the smoke particles. Smoke has a positive excess volumetric charge, the kinetics of which is typical for the smoke of each substance. References 7: 6 Russian; 1 Western.



**Phase Equilibria and Synthesis of Co-Cu-Cement Catalysts**

927M0185A Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian No 1,  
Jan 92 (manuscript received 18 Oct 90) pp 48-54

[Article by V.I. Yakerson, G.I. Frankfurt, Ye.A. Boyevskaya, A.L. Lapidus and Ye.Z. Golosman, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; UDC 547.21:542.97:66.094.222]

[Abstract] A battery of techniques was utilized in analyzing the phase equilibria and synthesis of Co-Cu-cement catalysts. The latter, intended for use in hydrocarbon conversion, were formed by mixing Co and Cu hydroxocarbonates with Talyum calcium-aluminum cement in aqueous ammonia. A cascade of exchange reactions during mixing was identified, in which the  $\text{CaAl}_2\text{O}_4$  component of the cement was more reactive than  $\text{CaAl}_4\text{O}_7$ . Among the identifiable phases were calcite, gybbsite and  $\text{Cu}(\text{OH})_2$ . Reactivity of the mixture increased in direct proportion to Cu concentration; at 9% by wt. Cu the CA phase Ca disappeared and maximum specific surface area was attained. Pyroprocessing at 400° C in air and under He followed by reduction in  $\text{H}_2$  at 800° C was accompanied by transition of  $\alpha$ -Co to  $\beta$ -Co and formation of solid solutions of Cu in  $[\text{g-}]$ Co and  $\text{Cu}^0$ . Compositions favoring maximum interactions of components in the early stages of mixing resulted in catalysts with maximum dispersity of CuO in  $\text{Co}_3\text{O}_4$ . Figures 2; tables 3; references 4 (Russian).

**Assessment of Co-MgO-Zeolite Catalysts by Thermoprogrammed Reduction, Desorption and IR Spectroscopy**

927M0185B Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian No 1,  
Jan 92 (manuscript received 05 Feb 91) pp 55-59

[Article by A.Yu. Krylova, A.L. Lapidus, S.D. Somin-skiy, L.F. Rar, A. Zukal, I. Ratkouski, M. Yanchalkova and V.I. Yakerson, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; Institute of Physical Chemistry and Electro-chemistry imeni I. Hejrovsky, Czechoslovak Academy of Sciences, Prague; UDC 541.128:548.737:543.422:546.623'73-36]

[Abstract] An analysis was conducted on the surface characteristics of Co(32%)-MgO(3%)-zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$ ) catalysts by thermoprogrammed reduction, CO desorption and IR spectroscopy. The results showed that the catalysts found suitable for Fischer-Tropsch synthesis embody Co represented by  $\text{Co}^{2+}$ , CoO,  $\text{Co}_3\text{O}_4$  and CoO-MgO solid solutions. Adsorption of CO to the catalytic surface was shown to involve activation and formation of a series of complexes with different binding energies. Figures 4; references 19: 10 Russian, 9 Western.

**Hydrocarbon Synthesis From CO and  $\text{H}_2$  on Co-Ru/- and Co-Pd/ $\text{Al}_2\text{O}_3$  Catalysts**

927M0185C Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian No 1,  
Jan 92 (manuscript received 24 Jun 91) pp 60-64

[Article by A.L. Lapidus, A.Yu. Krylova, M.P. Kapur, Ye.V. Leongardt, A.B. Fasman and S.D. Mikhaylenko, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; UDC 541.128:546.73:542.91:547.21]

[Abstract] An assessment was made of the impact of addition of 0.1-0.5% Pd or Ru to 10%Co/ $\text{Al}_2\text{O}_3$  catalysts on their efficiency and selectivity in Fischer-Tropsch syntheses. The results demonstrated that introduction of Pd enhanced both CO conversion and yield, particularly of  $\text{C}_3+$  hydrocarbons with a selectivity on the order of 57%. Introduction of Ru increased selectivity to a maximum of 81%. The liquid hydrocarbons consisted largely of alkanes, the exact composition of the products depending on the nature of the catalyst. For example, with 0.5% Pd or Ru catalysts the yield of n-paraffins rose to 70-75%. Figures 2; tables 2; references 6: 3 Russian, 3 Western.

**Structure and Catalytic Activity of Carrier-Immobilized Metal Complexes. Part 5. Immobilized Rh(II) Complex-Catalyzed Hydrodehalogenation of p-Bromotoluene by Reducing Agents**

927M0185D Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian No 1,  
Jan 92 (manuscript received 10 Dec 90) pp 65-71

[Article by V.I. Isayeva, Zh.L. Dykh, L.N. Lafer, V.I. Yakerson and V.Z. Sharf, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; UDC 541.128:541.49:546.97:542.944.7:547.539.3]

[Abstract] IR spectroscopy was used in assessing structural factors responsible for the efficiency of immobilized Rh(II) complexes in promoting hydrodehalogenation of p-bromotoluene by sodium hydrobromide and 2-propanol.  $[\text{Rh}_2(\text{O}_3\text{CCH}_3)_4]$  (I) immobilized on  $[\text{g-}]$ aminopropyl coupled silicagel (II) was observed to be the most efficient catalyst, exceeding other catalysts by a factor of ca. 60- to 166-fold. The latter included  $\text{Na}_4[\text{Rh}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]$ ,  $[\text{Rh}_2(\text{CH}_3\text{CN})_8(\text{H}_2\text{O})_2]$  and  $[\text{Rh}_2(\text{X})_4(\text{H}_2\text{O})_2]$  ( $\text{X}$  = hexafluoroacetylacetone) on II, polymers coupled with 3(5)-methylpyrazole and imidazole groups, as well as I on the latter carriers. The efficiency of the I-II combination was attributed to retention of the structure of I and insusceptibility of II to degradation by the reducing agents, particularly sodium borohydride. In other cases loss of efficiency was attributed to Rh-Rh bond disruption due to ligand replacement by carrier amino groups and degradation of the supporting matrix. Figures 3; tables 1; references 14: 9 Russian, 5 Western.

**Synthesis of C-Alkylimidazoles on Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts**

927M0187C Moscow IZVESTIYA ROSSIYSKOY AKADEMII NAUK: SERIYA KHIMICHESKAYA in Russian No 4, Apr 92 (manuscript received 06 Mar 91) pp 932-940

[Article by K.M. Gitis, G.Ye. Neumoyeva, N.I. Rayevskaya, G.A. Arutyunyan and G.V. Isagulyants, Institute of Organic Chemistry imeni N.D. Zelinskiy, Russian Academy of Sciences, Moscow; UDC 547.781.2+547.781.3+66.094.187+66.095.252]

[Abstract] Dehydrocyclocondensation of diamines with carboxylic acids (1:1) on bimetallic Pt/Al<sub>2</sub>O<sub>3</sub> (0.6% Pt) catalyst with H<sub>2</sub>:diamine molar ratios of 1-5:1 and temperatures of 280-400°C was found to be a successful approach to synthesis of a series of C-alkylimidazoles. Specifically, imidazole, 2-methylimidazole, 2,4(5)-dimethylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-hexylimidazole, 2-heptylimidazole and 2-undecylimidazole were prepared in yields of 15-95%. Detailed analysis of the factors affecting synthesis of 2-methylimidazole was conducted with respect to reactant ratios, temperature, reaction time, and hydrogen concentration in order to define conditions that could be used to optimize this process. Figures 2; tables 3; references 19: 3 Russian, 16 Western.

**Reaction of Furans with Hydrogen Peroxide in Presence of Vanadium Catalysts**

927M0225A Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 11(293), Nov 91 (manuscript received 22 May 89, after rework 4 Mar 91)pp 1462-1467

[Article by V. V. Poskonin, and L. A. Badovskaya, Krasnodarskiy Polytechnic Institute, Krasnodar 350072; UDC 547.724:546.215'881.5]

[Abstract] The reaction of furan, furfural, 5-nitrofurfural, 5-bromofurfural, furan-2-carboxylic acid, and 3-furfuryl alcohol with a H<sub>2</sub>O<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> system was investigated. The primary product observed was the 5-hydroxy-2(5H)-furanone, with maleic and fumaric acids and 2(5H)-furanone present as secondary products. Furfural and its derivatives formed mostly formic acid, while CO<sub>2</sub> was evolved from furan-2-carboxylic acid. Succinic acid and 2(3H)-furanone were not formed. In the presence of polyphenols the yield of the major product was increased but the reaction rate decreased. EPR established the presence of C-radicals in the reaction mixture. Experiments with furfural and 2-propanol demonstrated the reactivity of furfural toward radicals. The results indicate that oxidation proceeds via reaction of the furan ring with a hydroxy radical. Isolation of the

2,4-dinitrophenylhydrazone dialdehyde of maleic and fumaric acids from the reaction mixture indicated that the reaction proceeds primarily through dihydroxyfuran and dialdehyde intermediates, however some monohydroxyfuran is also formed. Some oxidation may also proceed by a nonradical mechanism. References 23: 11 Russian, 12 Western.

**The Thermal Desorption of Methanol From the Surface of a Vanadium-Antimony Catalyst as a Function of Its Pretreatment**

927M0247C Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 35 No 4, Apr 92 (manuscript received 11 Sep 91) pp 69-73

[Article by N.A. Osipova, T.V. Lazareva, and N.N. Sudakova, Physical Chemistry Department, Tomsk State University; UDC 541.128.13]

[Abstract] An experiment was conducted to determine the change in the spectrum of the temperature-programmed desorption of methanol from the surface of a vanadium-antimony [V-Sb-O] catalyst as a function of adsorption temperature and degree of filing and reduction of the catalyst's surface. The study catalyst, which contained 20% Sb<sub>2</sub>O<sub>4</sub> and 80% V<sub>2</sub>O<sub>5</sub>, was synthesized by impregnating analysis-grade antimony trioxide and roasting it for 4 hours at 500° C. Oxidized catalyst surfaces were produced by treating the surface in an O<sub>2</sub> flow at 450° C for 4 hours and then blowing in helium. Reduced catalyst surfaces were produced by processing the catalyst in methyl alcohol for 1 hour at 450°C. The metering of the methanol into the helium flow was performed through the vaporizer of a chromatograph so that the catalyst surfaces would be 30% filled with the alcohol. In those experiments where maximum filling of the catalyst surface with the alcohol was required, the degree of surface saturation was monitored by the constancy of the area of the methanol peak in the temperature-programmed desorption spectrum and in the desorption products before the programmed heating was begun. The temperature-programmed desorption of methanol was found to be accompanied by a complex redox process that included complete and partial oxidation of the methanol and the formation of surface oxidized forms, the decomposition of those forms, desorption of the untransformed alcohol, and the reduction and oxidation of the catalyst surface. Water was found to have a modifying effect on the state of the active centers on the catalyst surface. Specifically, water increased the catalyst surface's capacity for chemisorption of methanol and resulted in increased amounts of formaldehyde and carbon oxides in the desorbate. Ammonia blocked the centers of adsorption of methanol in both weakly and highly bound forms. Figures 3, table 1; references 6: 5 Russian, 1 Western.



**Complex Metal Compounds—Catalysts of Processes of Removing Toxic Impurities From Gases***927M0254A Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 7, Jul 92 (manuscript received 24 Feb 92) pp 750-759*

[Article by V.A. Golodov, Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy, Republic of Kazakhstan Academy of Sciences; UDC 541.49:541.128.12]

[Abstract] At present, the use of complex metal compounds as the precursors of catalysts for removing toxic impurities from waste and process gases at enterprises is not very widespread. The use of complex metal compounds for such purposes is continually increasing, however. Most of the research in this field is being done at the Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy of the Republic of Kazakhstan Academy of Sciences. The complex metal catalysts that are being developed based on phosphine ( $\text{PH}_3$ ), arsine ( $\text{AsH}_3$ ), and hydrogen sulfide ( $\text{H}_2\text{S}$ ) appear especially promising. According to the mechanism that has been proposed to explain the effect of complex metal catalysts, the catalyst-ions abandon the inner sphere after their oxidation. The initial state of the complex ion is then regenerated as a result of further transformations of the ligands. An intrasphere redox reaction involving the formation of an active radical (for example,  $\text{Cl}^\bullet$ ) with subsequent transfer of the electron to it from a donor (molecules of the substrate [ $\text{Ph}_3$ ,  $\text{AsH}_3$ ,  $\text{SO}_2$ , etc.] is also possible in the case of several ligands. Complex compounds of  $\text{Cu(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Mn(VII)}$ ,  $\text{Ce(IV)}$ , and  $\text{Cr(VI)}$  with haloid or sulfate ligands have also been shown to be active oxidizing agents in reactions with hydrogen sulfide. Haloid compounds of  $\text{Ph(II)}$  have proved to be the most active in the oxidation of CO, and metal complexes with an intermediate degree of oxidation have been shown to be active catalysts of the transfer of CO molecules. Systems in which CO is oxidized without an intermediate oxidizing agent have also been found. The technique of attaching complexes on the surface of solid carriers has opened new possibilities regarding removing toxic impurities from waste and process gases. Localization and stabilization of one or two bonds of the central atom with the surface atoms of the carrier have both been shown to be important in the theory of systems of metal complexes and in coordination compound chemistry proper. References 59: 40 Russian, 19 Western.

**The Use of Catalysts in the Process of Producing Resins With an Elevated Molecular Mass***937M0011D Moscow PLASTICHESKIYE MASSY in Russian No 1, Jan 92 pp 41-43*

[Article by M.S. Klebanov, K.N. Likhoded, G.A. Musiyenko, and T.N. Kravchuk; UDC 678.686.044]

[Abstract] Epoxy resins are among the most promising forms of synthetic resins, and the most promising among

the latter are polyepoxy resins with an elevated molecular mass obtained by reacting low-molecular epoxy resins with polyhydroxyl-containing compounds. When the epoxy resins or polyhydroxyl-containing compounds also contain halogen, it is possible to produce refractory polymers. Such resins are produced in a solvent or without one in the presence of a catalyst. Onium compounds, especially phosphonium and quaternary ammonia compounds and hydroxides of alkaline and alkaline earth metals, are used most widely as catalysts of the process. Such compounds have been shown to result in colorless epoxy resins with improved performance properties. Organic metal, especially organic tin, catalysts appear to be especially promising and have been used successfully to produce highly pure resins with a low amount of coloring and good stability during storage. There is a rather wide variety of catalysts that may be used to produce epoxy resins with an elevated molecular mass. Some individual catalysts and even some entire classes of catalysts have shortcomings that must be taken into account, however. It is, for example, inadvisable to use organic and inorganic halides as catalysts because they dissociate upon dissolution in the reaction mixture and form halogen ions that in turn impart color to the resultant epoxy resins. It is also inadvisable to use hydrides of alkaline and alkaline earth metals on a commercial scale because of the high explosion hazard that they pose. In the final analysis, the selection of a catalyst for producing epoxy resins with an elevated molecular mass must be dictated above all by the set of properties required in the final product. References 64: 14 Russian, 48 Western.

**Production of Zeolites With High Silicon Content and Catalysts Based on Them***937M0020A Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 2-7*

[Article by B. K. Nefedov, All Union Scientific Research Institute of Petroleum Processing; UDC 547.53:661.183.6]

[Abstract] Synthesis of zeolites is a complex process requiring accurate control of many parameters. The only industrial production method is based on hydrothermal crystallization of alkaline aluminum silicate compositions in aqueous medium at a temperature range of 120-200° C and under pressure. The type of zeolite, its structure and chemical composition, morphology and the crystalline size are determined by crystallization conditions and by the composition of the reaction mixture. In this paper a review of predominantly western literature was presented concentrating on the effect of various parameters in the final product: aluminum content in the starting gel, the degree of its dilution, the nature and quantity of inorganic base and of the organic cation used, effect of the mineralization agent and of the nature of silicon containing crude. Tables 2; references 51: 20 Russian (14 by Western authors), 31 Western.

### **Zeolite-Y, a Component of Catalysts for Petroleum Fractions Hydro-Purification**

937M0020B Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian* No 3, Mar 92 pp 7-12

[Article by B. K. Nefedov, R. R. Aliyev, All Union Scientific Research Institute of Petroleum Processing; UDC 547.53:661.183.6]

[Abstract] Due to their unique properties, zeolites are considered important catalysts in petroleum processing. However, literature data are limited on the role of zeolite in formation of the structures and active phases of the Al-Ni(Co)-Mo compositions. Previous studies showed that zeolites are modifiers of such structures and of the acidity of reagents affecting their interaction among themselves and with the carrier. In present paper experimental results were reported on studies of the mechanism of zeolite modification of hydro-purification catalysts based on IR spectroscopy, thermogravimetry, x-ray spectroscopy, x-ray photoelectronic microscopy, EPR, combined dissipation and electronic diffusion reflection spectroscopy data. The following aspects were covered: interaction of aluminum oxide with zeolite and with hydrogenating components; effect of zeolite-Y on physical-chemical properties of Al-Ni-Mo system and effect of the cationic forms of zeolite-Y on the formation of hydrogenating phases in that system. The data showed that the promoting action of zeolite-Y relates to the following: change in the porous structure of the catalyst resulting in an increased fraction of the micropores; blockage of the penetration of Ni and Mo ions into the carrier mass resulting in a decrease of catalytically inactive compounds; increased number and of the degree of dispersion of the surface active phases Al-Ni-Mo and Ni-Mo. Characteristics of selected zeolite containing catalysts for hydro-desulfurization of kerosene and diesel fractions were tabulated. These catalysts made it possible to lower the temperature of various processes by 20-35°; they increased the productivity by 10-15% (relative), they increased the inter-regeneration performance period of the catalyst to 2-3 years and the overall service period of these catalysts to 6-7 years. Tables 5; figures 7; references 19: 16 Russian (2 by Western authors), 3 Western.

### **Active Surface Centers and Catalytic Properties of Iron Containing Pentasils**

937M0020C Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian* No 3, Mar 92 pp 15-17

[Article by Ye. Ye. Knyazeva, G. M. Telbiz, N. F. Meged, T. V. Limova, Groznyy Petroleum Institute imeni Academician M. D. Millionshchikov; UDC 541.128.13 + 549.67-44 + 542.949.4 + 542.951.1]

[Abstract] Pentasils are promising catalysts for synthesis and processing of alkyl-aromatic hydrocarbons. In present work functional surface groups and catalytic properties were investigated of pentasils modified with iron either entirely (Fe-Si) or partially (Fe-Al-Si). Their

catalytic activity was studied on conversions of n-hexane and n-octane at 500-600° C. Such substitution led to a change in activity and selectivity of the catalyst. The activity decreased in the order: Al-Si > Fe-Al-Si > Fe-Si, while the yield of aromatic hydrocarbons increased as follows: Fe-Si < Al-Si < Fe-Al-Si. An increase in temperature improved the activity of these reagents. The specific actions of these catalysts may be the result of the combination of active centers: the Bronstedt's centers resulting from isomorphic substitution  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  by  $\text{Fe}^{3+}$ ; or by Lewis centers related to external  $\text{Fe}^{3+}$ , or by hydro-dehydrogenating centers forming by the reduction of  $\text{Fe}^{3+}$  ions. Tables 3; figures 2; references: 5 (Russian).

### **Production of Alkylaromatic Hydrocarbons on High Silicon Content Zeolite Containing Catalysts**

937M0020D Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian* No 3, Mar 92 pp 20-23

[Article by S. P. Chernykh, K. G. Ione, P. S. Chekriy, G. L. Bitman, A. S. Loktev, V. N. Romannikov, L. A. Makhlis, G. P. Snytnikova, V. A. Porollo, A. N. Spektor, Siberian Division of All Union Scientific Research Institute; Institute of Catalysis, Siberian Division of Russian Academy of Sciences; UDC 547.53:661.183.6]

[Abstract] Zeolite catalysts with high content of silicon are normally used in production of alkylaromatic hydrocarbons with high isomeric purity. These catalysts are highly selective, easily regenerated, they produce little tar and are non-corrosive. The advantages of these catalysts were demonstrated by synthesis of 1,2,4,5-tetramethylbenzene (Durol), p-ethyltoluene, p-diethylbenzene and by more general reactions of alkylation of benzene with propylene and alkylation of bicyclic aromatic hydrocarbons. In all cases conditions were optimized to yield isometrically pure products with high selectivity and satisfactory productivity with minimal side reactions. Tables 5; figure 1; references 23: 20 Russian (8 by Western authors), 3 Western.

### **Aromatization of Condensed Gas Benzene Fractions and Petrochemical Gasses on Zeolite Containing Catalyst**

937M0020E Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian* No 3, Mar 92 pp 23-24

[Article by N. N. Rostanin, L. D. Konovalchikov (Deceased), Ye. D. Rostanina, A. G. Vorotnikov, B. K. Nefedov, V. G. Leontiyevskiy, All Union Scientific Research Institute of Petroleum Processing, Production Cooperative "Katrani", Moscow Scientific Technical Cooperative "Katalizator"; UDC 547.53:661.183.6]

[Abstract] Zeolite catalysts of the pentasil group have the unique capability of converting lower paraffins and olefines into higher molecular weight products through oligomerization and dehydrocyclization. Several catalysts for aromatization of aliphatic hydrocarbons were

developed producing up to 90.7% yields of valuable aromatic hydrocarbons. Another example of this catalyst's activity was provided by aromatization of benzene fractions of gaseous condensates from the crude "Tat-neft" material. The quality of the product appeared to be related to the starting material. Tables 5.

#### **New Directions for Utilization of SGK-1 Catalyst**

937M0020F Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 26-27*

[Article by N. P. Moreva, Z. K. Olenina, Yu. P. Yasyan, A. Yu. Adzhiyev, All Union Scientific Processing Institute Gazpererabotka; UDC 665.632.074.3]

[Abstract] Production of domestic zeolites with high content of silicon made it possible to develop new catalysts for petrochemistry and petroleum processing. These zeolites preserve their crystalline structure up to 1100° C in air up to 12 hrs; they are resistant to acid media and do not clog up with coke as other zeolites. Their use in extrusive petroleum processing was investigated showing them to be highly effective in catalytic cracking, in hydro-refining of direct distillation benzene and refining products, in isomerization of xylene and selective deparaffinization of fuel and oil fractions. Experiments were carried out with this type catalyst to purify petroleum gas from sulfur compounds at a temperature range of 100-300° C. Already at 160° C the conversion was 92.8% and at 300° C an almost complete conversion of ethylmercaptan to hydrogen sulfide was achieved. In another run this catalyst was used effectively in hydrolyzing carbon sulfate to hydrogen sulfide and carbon dioxide. Tables 3; references: 4 (Russian).

#### **Zeolite Containing Catalyst for Organic Synthesis and Production of High Octane Benzene**

937M0020G Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 30-31*

[Article by N. N. Rostanin, L. D. Konvalchikov (Deceased), A. S. Shtefan, Ye. D. Rostanina, B. K. Nefedov, All Union Scientific Research Institute of Petrochemical Processing; UDC 665.73:66.097.13]

[Abstract] A domestically produced catalyst KM-125, based on a zeolite with high content of silicon TsVM, was used effectively in processing methanol and its byproducts as well as olefin containing waste gases from chemical and petroleum processing plants into liquid hydrocarbons, components of high octane gasoline. The same catalyst could be used for production of  $\alpha$ -olefines from  $C_2$ - $C_3$  alcohols and for production of Durol. This should provide the starting material for industrial production of pyromellite dianhydride and polymers derived from it. The selectivity of this process is in the range of 70-79%. Tables 5; references 2: 1 Russian, 1 Western.

#### **Hydroisomerization of Alkanes and Benzene Fractions Over Mordenite Containing Catalyst**

937M0020H Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 31-33*

[Article by V. G. Ryzhikov, A. A. Kamenskiy, V. I. Tarasov, V. A. Tremasov, Ye. M. Terekhin, V. M. Savina, Novokuybyshev Branch of Siberian Division, All Union Scientific Research Institute, Novokuybyshev Petroleum Processing Plant; UDC 665.73:66.097.13]

[Abstract] The goal of this work was to evaluate hydroisomerization of  $C_5$ - $C_7$  n-alkanes and benzene fractions over a heterogeneous catalyst Pt-NM (modulus  $m=1.75$ )/ $\gamma$ - $Al_2O_3/B_2O_3$  (with a Cl promoter). This catalyst (LI-C56) was active in hydroisomerization of N-alkanes in a middle temperature range with a selectivity of 82-93%. Elevating the temperature lowered the yield of the isomers but increased the hydrocracking products. Overall, the KI-C56 catalyst obtained from boron oxide promoted  $\gamma$ - $Al_2O_3$  with a chlorine modifier made it possible to isomerize  $C_5$ - $C_7$  n-alkanes in one passage at middle range temperatures. The octane number of this isomerization product reached 82-85 points. Tables 4; figure 1; references: 10 (Russian).

#### **Effect of Activation Method on Properties of Zeolite Containing Hydropurification Catalysts**

937M0020I Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 33-34*

[Article by S. I. Glinchak, Yu. A. Yegorov, R. R. Aliyev, Ye. D. Radchenko, B. K. Nefedov, N. A. Grigoryev, All Union Scientific Research Institute of Petroleum Processing, Production Organization "Gorknefteorgsintez"; UDC 547.53:661.183.6]

[Abstract] One of the methods of obtaining effective catalysts for hydropurification processes involves the use of zeolite containing composites. Introduction of zeolite into Al-Ni-Mo matrix changes its structure, increases the quantity of catalytically active components, while decreasing the level of inactive ones; it increases the dispersion of active phases and promotes thermal stability of these samples. Several catalysts were prepared and the effect of the activation methods on their activity was investigated. It was shown that the activity and stability of catalysts increased by treatment with sulfur containing compounds, especially elemental sulfur and hydrogen sulfide. The economic savings at a single hydropurification plant was about 250,000 rubies per year. Tables 3; figure 1; references: 3 (Russian).

#### **Catalyst for Desulfurization of Diesel Fuel With Heavy Fractional Composition**

937M0020J Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 92 pp 34-35*

[Article by P. G. Bannov, G. Ye. Shumilova, N. A. Voronina, O. V. Yurkina, T. F. Alekseyenko, Production Organization "Kirishinefteorgsintez"; UDC 547.53:661.183.6]



[Abstract] A new, finely granulated catalyst GKD-202P containing zeolite was developed and used in desulfurization of heavy Diesel fuel with high sulfur content. The GKD-202P catalyst differed from the earlier GKD-202 counterpart by an absence of nickel and a lower content of molybdenum. Also, the method of introduction of hydrogenating metals was different. It was shown that this catalyst is capable of extensive hydrogenation of sulfur compounds producing Diesel fuel with sulfur content less than 0.2%. Tables 2; references: 3 (Russian).

#### **Effect of Potassium Carbonates on Steam Regeneration of Iron Catalysts**

937M0021A Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 92 p 12

[Article by A. D. Guseynova, L. M. Mirzayeva, N. Z. Muradov, R. Yu. Ganbarov, M. I. Rustamov. Institute of Petrochemical Industry imeni Yu. G. Mamedaliyev, Azerbaydzhan Republic Academy of Sciences; UDC 66.097.38]

[Abstract] Iron oxide catalysts are widely used in petroleum processing and in petrochemical syntheses. During the active process the catalysts are converted to various oxides ( $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ); coke is deposited on their surface and lowers their activity. They can be regenerated with air or with steam; the latter seemed to be a preferred method because it yields water containing gas as the end product. This regeneration process is accelerated by addition of  $\text{K}_2\text{CO}_3$ ; also the activity of  $\text{Fe}_2\text{O}_3$  based catalyst is increased and the iron-potassium catalysts facilitate gassification of carbon compounds that precipitate on their surface. Reference: 1 (Western).

#### **Colloidal-Chemical Model for Oil Tendency to Form High Temperature Deposits**

937M0021B Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 92 pp 15-17

[Article by V. L. Lashkhi, G. I. Shor. State Scientific Research Institute of Chemistry, All Union Scientific Research Institute of Petroleum Processing; UDC 665.7.038:621.431]

[Abstract] Based on colloidal-chemical concepts, the formation of carbon deposit may be viewed as a coagulation process which, depending on the conditions, may occur at different rates and which in the final analysis affects the sedimentation stability of the system. Coagulation occurs with introduction of relatively small quantities of electrolytes and it intensifies as their concentrations is increased. A mathematical model was presented for the coagulation rates starting from the assumption that the coagulation rate and the amount of deposits in high temperature zones depend on the coagulation rate constant and the stability factor. An assumption was expressed that coagulation intensification could be expected at a given concentration of the electrolyte in the system and a specific thickness of the diffusion layer. Identifying the electrolyte concentration change with the change of the dielectric permeability of the solution, and the change in the thickness of the diffusion layer with a change of its electroconductivity  $\lambda$ , the following function can be proposed:  $\epsilon/\lambda^{1/3} = \text{const}$ , where the constant has a characteristic value for each oil. This relationship was tested in an experimental setting. Figure 1; references: 3 (Russian).

#### **Effect of Alkyl Phenols on Colloidal Structure of Detergent- Dispersive Additives**

937M0021C Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 92 pp

[Article by K. D. Korenev, A. A. Gundyrev, M. L. Mukhin, N. Bennani, A. A. Zasavitskaya, State Academy of Petrochemical and Gas Industry imeni I. M. Gubkin; UDC 665.765-404.038.1:541.124]

[Abstract] The goal of this work was to continue the investigation of the intermolecular reactions of alkyl phenols present in salicylate and phenol additives and their active substances. The polarity of the studied components decreased in the order: calcium alkyl phenol sulfonate > calcium alkyl benzyl sulfonate > calcium alkyl salicylate +  $\text{CaCO}_3$  > calcium alkyl salicylate > alkyl benzyl sulfonate +  $\text{CaCO}_3$ . It was shown that these additives interact with the active substance and with each other via hydrogen bonding. The results depend on the type of additive (neutral or basic), on the concentration of alkyl phenols and on temperature. Various combinations of these factors result in stabilization or destabilization of the colloidal structure of oil additives. Figure 1; reference: 1 (Russian).

### Heat Conditions of the Oscillatory Flame Propagation Process at the Diffusion Combustion Threshold of Condensed Fuel

927M0252A Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 7, Jul 92 (manuscript received  
30 Jul 91) pp 974-976

[Article by V.I. Yeregin and V.I. Potyakin, All-Union Scientific Research Institute of Fire Protection, Balashkha; UDC 536.46]

[Abstract] An experimental study was conducted to examine the oscillatory flame propagation process occurring at the diffusion combustion threshold of condensed fuel. Polymethylmethacrylate was used as a condensed fuel, and its monomer methylmethacrylate, which is the main pyrolysis product of polymethylmethacrylate during combustion, was used to estimate the degree of effect of the cone-shaped phase. VR 5/20 tungsten thermocouples with 50- $\mu$ m-diameter wire were used to measure the temperature. The polymethylmethacrylate rods measured 10 mm in diameter and 70 mm in height. Before the experiments, the upper part of the rods was shaped so as to correspond to the cone of the pyrolysis zone of the cone-shaped phase formed during combustion in air, when the angle at the cone's vertex equals about 15°. The oscillation process was studied in a flow of nitrogen-oxygen mixture (with an oxygen concentration of 15.5 vol.-%) at a gas flow velocity of 1 cm/s. The change in flame temperature during the oscillation process at the combustion threshold was analyzed on the basis of oscillograms. The experiments confirmed the significant effect of the thermophysical properties of the cone-shaped phase on the characteristics of the oscillations. In the case of polymethylmethacrylate, the temperature at the points of the maxima decreased much more rapidly than occurs during near-threshold combustion of methylmethacrylate. The amplitude of the oscillations during combustion of the liquid monomer also increased much more slowly. The frequency of the oscillatory process remained unchanged at 8 Hz for the polymer and 6 Hz for the monomer. The polymethylmethacrylate's higher flame propagation rate was attributed to the fact that the temperature of the polymer's surface is much higher than the monomer's boiling point even close to the combustion threshold. Figures 2; references 8: 5 Russian; 3 Western.

### Structure of a Low-Speed Detonation Wave in Pyroxylin Powders

927M0252B Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 7, Jul 92 (manuscript received  
27 Feb 91) pp 977-982

[Article by V.F. Martynyuk, A.A. Sulimov, S.V. Chekanov, and M.K. Sukoyan, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 535.529+662.215.1]

[Abstract] The structure of the low-speed detonation wave occurring in filled charges of pyroxylin powders

under conditions of explosive initiation and its development from a convective combustion mode were studied by the optical method and by analyses of the pressure profiles recorded by piezoelectric sensors. VU<sub>ph</sub> 4/1 and VU<sub>ph</sub> 15/1 single-channel pyroxylin powders with cylindrical granules and effective grain sizes of 0.6, 1.66, and 3.35 mm and channel diameters of 0.1, 0.25, and 0.2 mm, respectively, were used in the studies. The granules of the VU<sub>ph</sub> powders had a phlegmatized surface layer ensuring that the detonation would be propagated at a constant speed detonation under the study conditions. The studies established that tens of microseconds are required for the pressure to build up to its maximum value. In all cases, reducing the size of the particles while maintaining comparable low-speed detonation wave propagation speeds and maximum pressure increased the time required for the maximum pressure to be reached. Analogously, in the case where the combustion was transformed into low-speed detonation, the time required to reach maximum pressure was greater than in the case of explosive initiation of the low-speed detonation wave. Simultaneous measurements of the waves' pressure (by piezoelectric sensor) and mass velocity (by the electromagnetic method) showed that the sensors recorded the pressure virtually synchronously even though the piezoelectric pressure exceeded the level of the hydrodynamic pressure. Rather lengthy pulses were noted on the pulse recordings before the onset of the sharp rise in pressure (or mass velocity). These pulses were linked to filtration of the gaseous products through the skeletons of the solid particles. In all cases the pressure front lagged behind the luminescence front, which is consistent with thinking regarding the advance filtration of gaseous products during the propagation of a low-speed detonation wave in highly porous charges of granular powders. Figures 3, tables 2; references 6 (Russian).

### The Structure of a Pressure Wave During Convective Flame Propagation in Charges With Different Porosities

927M0252C Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 7, Jul 92 (manuscript received  
28 Feb 91) pp 983-990

[Article by A.V. Romankov, A.A. Sulimov, M.K. Sukoyan, and M.S. Biryukov, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 662.215.1]

[Abstract] The dynamics of the process of convective combustion and the structure of the pressure wave in charges of pyroxylin powder were studied over a wide range of charge densities (800 to 1,400 kg/m<sup>3</sup> with porosities ranging from 50 to 12%) under conditions of rapid pressure increases to 250 MPa. The porous charges were made of grains of 5/1 pyroxylin powder in the shape of a single-channel cylinder with an outer diameter of 1.4 mm and length of 3 mm. To control the convective combustion process, the researchers applied inert materials to the outer surface of the starting granules. The



inert materials (inhibitors) were kept from getting inside the grain channels. T-6000 high-frequency piezoquartz sensors were used to measure the gas pressure in the free space, and photodiode sensors were placed diametrically opposite the piezoquartz sensors and used to record the luminescence (flame) propagation front. OK-40 and DL-2000 multichannel oscillographs were used to record the signals from the piezoelectric and photodiode sensors. The studies established that one of two types of convective combustion propagation modes could exist depending on the nature of the change in flame speed and pressure over time. Specifically, three nonstationary modes and one quasi-stationary mode could exist. The three nonstationary modes could be classified as follows: accelerating (i.e., flame propagation increases in speed as the pressure in the flame front increases); stabilized (the propagation rate is nearly constant while the pressure in the flame front increases); and attenuating (the convective combustion propagation rate decreases despite an increase in pressure in the flame front). In the quasi-stationary mode, when the pressure in the outer space and in the convective combustion front are constant, the flame is propagated at a speed that remains constant along the length of the charge. Specific examples are used to illustrate the critical conditions of the existence of each of these different convective combustion propagation modes. A mechanism of stabilizing convective combustion is proposed that is based on sealing and reducing the gas permeability of the charge before the flame front. Figures 4, table 1; references 10: 6 Russian, 4 Western.

#### The Properties of Strong Shock Waves in Monoatomic Gases

927M0252F Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 7, Jul 92 (manuscript received  
31 May 91) pp 1013-1020

[Article by S.A. Yegorushkin and V.S. Uspenskiy,  
Moscow State University imeni M.V. Lomonosov; UDC  
533.6.011.72]

[Abstract] A theoretical study was conducted to determine the possibility that a strong shock wave in a monoatomic gas will effect a transition into a neutrally stable state. The study was based on a model of a monoatomic gas that considered partial ionization and the excitation of energy levels. The analysis demonstrated that a transition to a state of neutral stability is possible in narrow oncoming-flow Mach number ranges corresponding to the onset of primary, secondary, etc., ionization. The reasons for the transition of a strong shock wave to an unstable state owing to the effect of anomalous relaxation outpacing radiation and nonlinear effects are discussed. It is noted that in the latter two cases a transition to an unstable state may occur in the case of shock waves satisfying the conditions of neutral

stability within the framework of the classical Dyakov-lordanskiy theory. It is hypothesized that the mechanism of the transition of a shock wave to a neutrally stable state is linked to the equilibrium pumping of the highly excited (Rydberg) portion of the spectrum of the excited atom or ion. The existing experimental data were said to be insufficient for any definitive conclusion regarding the applicability of the proposed mechanism of the occurrence of a mode of neutral stability. The hypothesis advanced regarding the effect of the excited electron levels of atoms and ions on shock wave stability thus needs further experimental verification. Figures 4; references 22: 16 Russian, 16 Western.

#### Kinetics of Evaporation of a Drop of Water in Hydrocarbon Flames

937M0016B Kiev *FIZIKA AERODISPERSNYKH*  
in Russian N 33, Mar 90 (manuscript received  
26 Jan 87) pp 22-24

[Article by G. A. Mokhov, senior scientific associate, V. V. Kalinchak, candidate of physico-mathematical sciences and G. A. Petropavlovskaya, student; Odessa University; UDC 536.46]

[Abstract] Model studies of the kinetics of evaporation of a single drop of water placed in different points of a flame of a drop of liquid fuel used ethanol, acetone and octane flames. Results obtained according to the evaporation constant were compared with temperature profiles in the flame. An assumption concerning the effect of the composition and temperature of products of combustion on the kinetics of evaporation of a drop of water in the flames was described and discussed. Figures 3; references 3 (Russian).

#### Effect of Thermophoresis on Motion of Particles and Velocity of Flame in Gas Suspensions

937M0016C Kiev *FIZIKA AERODISPERSNYKH*  
*SISTEM* in Russian No 33, Mar 90  
(manuscript received 10 Oct 88) pp 59-64

[Article by S. V. Goroshin, candidate of physico-mathematical sciences and Yu. L. Shoshin, scientific associate; Odessa University; UDC 536.46]

[Abstract] A study of the effect of thermophoresis on the motion of solid particles in the front of a laminar flame showed that the thermophoretic force for particles of micron dimensions is comparable to the viscosity force and may lead to their damping in the Michaelson zone of the flame. The study showed that thermophoresis amplifies the dependence of the velocity of the flame on the dispersivity of the gas suspension for particles with diameter less than 5 microns during both diffusion and kinetic regimes of combustion of particles. Figures 3; references 7: 6 Russian; 1 Western.

**Electrochemical Oxidation of 1,3-Diketones in Hydrohalic Acid Salts**

927M0185E Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian No 1,  
Jan 92 (manuscript received 15 May 91) pp 154-158

[Article by M.N. Elinson, T.L. Lizunova and G.I. Nikitin, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow; UDC 541.138.2:542.971.2:547.442:547.443]

[Abstract] Ongoing studies were continued on electrochemical oxidation of 1,3-diketones in hydrohalic acid salts under conditions designed to provide maximum dimer yield and/or conversion. Electrolysis of acetylacetone with NaI mediator in acetone, acetonitrile or methanol resulted in the synthesis of 3,4-diacylhexane-2,5-dione in yields approaching 90%. Under analogous conditions 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione—with NaI or NaBr mediator in acetone, MeCN or MeOH—were converted to 2-iodine or 2-bromine substituted 1,3-diketones in yields reaching 90%. Tables 2; references 8: 2 Russian, 6 Western.

**Electrochemical Study of High-Temperature Superconductor Oxides With a Different Type of Conductivity**

937M002A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 128 No 1, Jul 92 (manuscript received  
23 Mar 92) pp 84-87

[Article by M. A. Bondarenko, T. N. Koltsova, V. V. Seriyevskiy, T. N. Adrianova, and Corresponding Member of the Russian Academy of Sciences A. N. Kholkin, Moscow Engineering-Physics Institute, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Russian Academy of Sciences, Moscow; UDC 543.538.955+539.2]

[Abstract] Superconductors of the formulas  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Bi}_{1.85}\text{Ce}_{0.15}\text{CuO}$  samples were studied by inversion volt-ammeter and no-power chronopotentiometry methods in an attempt to develop methods for studying and testing high-temperature superconductors at normal temperatures. For comparison, samples of a ceramic of the composition  $\text{Bi}_2\text{CaSr}_2\text{Ca}_2\text{O}_{8.8}$  were also studied. The Bi and Y ceramics are both p-type high-temperature superconductors. Two cathode and anode peaks were observed in the volt-amperegrams of both Y and Nd superconductors due to oxidation-reduction processes involving Cu ions. Peaks of the volt amperegrams of Y samples having low-temperature superconducting properties have a lower intensity than the peaks of a ceramic not possessing a superconducting transition. A reverse relationship is observed in the intensity of Nd peaks. The chronopotentiometric data also show a difference in the behavior of p-type and electron-conducting superconductors. The initial potential of superconducting samples is less positive than that of nonsuperconducting. The numerous differences in chronotensiograms of Y and Nd samples may be related to differences in the type of carriers. References 9: 6 Russian, 3 Western

**Light Scattering by ZnSe Polycrystals Chemically Precipitated From Gaseous State**

927M0186A Moscow VYSOKOCHISTYYE  
VESHCHESTVA in Russian No 1, Jan-Feb 92  
(manuscript received 16 Sep 91) pp 7-11

[Article by G.G. Devyatykh, V.I. Bredikhin, Ye.M. Gavrishchuk, I.A. Korshunov, S.P. Kuznetsov and V.S. Okunev, Institutes of Chemistry of Highly Purified Substances and of Applied Physics, USSR Academy of Sciences, Nizhniy Novgorod; UDC 535.375.54]

[Abstract] Light scattering was evaluated for suitability in assessing surface imperfections in ZnSe polycrystals. Test samples were obtained by precipitation from the gaseous state by hydrogen selenide and compression of the precipitate into 40 mm x 5 mm tablets at high temperature and constant pressure (1050° C, 200 MPa, 1 h). Plots of scatter angle (20-140°) of He-Ne laser beams (0.6328  $\mu$ ) vs. intensity were correlated with evidence of surface defects obtained by microphotography. A test sample revealed  $10^8$  cm<sup>-3</sup> 0.6  $\mu$  defects, demonstrating the sensitivity and practical usefulness of this approach. Figures 5; references 10: 8 Russian, 2 Western.

**Preparation of Highly Purified Phosphorus Oxychloride for Fiberoptic Applications**

927M0186B Moscow VYSOKOCHISTYYE  
VESHCHESTVA in Russian No 1, Jan-Feb 92  
(manuscript received 03 Dec 90) pp 44-55

[Article by M. Sybr and Z. Plzk, Rzhzh [sic]-by-Prague; UDC 66.048.32:547.412.133(546.185'131-31:546.05:681.3)]

[Abstract] Problems related to purification of phosphorus oxychloride (PO) intended for fiberoptic technology were assessed vis-a-vis its hygroscopic properties and absorption of chlorinated hydrocarbons and transition metal chlorides. Extensive studies led to the demonstration that UV photochlorination was effective in reducing the concentration of organic impurities and OH groups in PO samples. In addition, determination of liquid-gas partition coefficients indicated that elimination of 1,1,2-trichloroethane poses a special problem requiring further efforts. In general, however, the most effective techniques for removal of transition metal chlorides and organic impurities consisted of a combination of redistillation and cold distillation with preliminary photochlorination of OH- and CH-bearing impurities. Figures 4; tables 5; references 27: 9 Russian, 18 Western.

**Polytetrafluoroethylene Surface Impurities**

927M0186C Moscow VYSOKOCHISTYYE  
VESHCHESTVA in Russian No 1, Jan-Feb 92  
(manuscript received 11 Nov 90) pp 93-98

[Article by A.M. Yaroshenko, L.A. Vasilyev, G.Z. Blyum and Ye.A. Ryabenko, All-Union Scientific Research

Institute of Chemical Reagents and Highly Purified Chemical Substance, Moscow; UDC 546.131+54.482]

[Abstract] Scanning electron microscopy and photoelectron spectroscopy were employed in assessing efficacy of conventional techniques for washing polytetrafluoroethylene (Teflon) products. The study demonstrated that polytetrafluoroethylene absorbs hydrocarbons and sequesters Cl atoms in surface pores, fissures and other defects. Commonly employed conventional techniques of washing with highly purified water were inefficient in removing impurities and contaminants. However, dense samples of polytetrafluoroethylene with fewer and smaller surface defects were far less likely to be contaminated with Cl atoms, suggesting one approach to product improvement. Consequently, despite its impressive chemical stability, polytetrafluoroethylene products are subject to contamination with hydrocarbons and chlorine and improved methods of purification need to be developed for the lower density products. Figures 5; references 2 (Russian).

**Special Features of the Vulcanization of Elastomers in Latexes and Materials Based on Them**

927M0247A Ivanovo IZVESTIYA VYSSHIKH  
UCHEBNYKH ZAVEDENIY: KHIMIYA I  
KHIMICHESKAYA TEKHOLOGIYA in Russian  
Vol 35 No 4, Apr 92 (manuscript received 13 Sep 91)  
pp 3-18

[Article by I.D. Khodzhayeva, Department of the Chemistry and Physics of Polymers and Polymer Processing, Moscow Institute of Fine Chemical Technology imeni M.V. Lomonosov; UDC 678.061]

[Abstract] The vulcanization of elastomers by using various sulfur accelerating systems is the most accessible and widely used (both in the former Soviet Union and abroad) cross-linking method of producing elastomers that will in turn be used to produce a final material with the required set of performance properties after its reticulate structure has been formed. The cross-linking may be performed either in the final stage of producing products or directly in the latex. A review of published and experimentally obtained data on cross-linking elastomers in aqueous dispersions indicates that the process should be classified as a heterogeneous topochemical process because the reacting materials are in different phases and the reaction between them occurs primarily at the interface where most of the polymer material is concentrated. Surfactants in the form of emulsifiers of aqueous dispersions play a decisive role in the process of transferring the components of the cross-linking system from the aqueous phase into the polymer phase thanks to the effects of solubilization and micelle formation in the adsorption layers. The use of sulfur-accelerating cross-linking systems creates the prerequisites for the formation within the elastomer globules of a heterogeneous network with a density that diminishes from the periphery to the center. The reaction of cross-linking an

elastomer in an aqueous dispersion may be slowed and controlled in any stage, which thus makes it possible to determine the effect of the degree of the polymer's intraglobular transformation on the structure, properties, and subsequent processing of the material and to determine the optimal reaction conditions. Films produced from dispersions of elastomers in which a cross-linking reaction occurs have a macroheterogeneous globule structure, with the degree of coalescence depending on the nature of the polymer, the type and concentration of surfactant, and the depth of interglobular transformation of the polymer. All else being equal, the latter factor has a particularly strong effect on the strength properties and permeability of the film produced. Elastomers may also be cross-linked in materials based on aqueous dispersions. SKI-3 is a dispersion that has received particular attention in the literature. Mixtures of SKI-3 and SKS-30 butadienestyrene latex have been shown to result in materials that are stronger than natural latex. Materials based on the elastomers BK and SKEPT are distinguished from the standpoints of gas permeability and thermal oxidation stability. Figures 10, tables 5; references 50: Russian, Western.

#### **MoS<sub>2</sub> Colloidal Semiconductors With a Quantum Dimensional Effect. Determination of Dimensions by the Optical Method**

927M0252D Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 11 No 7, Jul 92 (manuscript received 12 Jul 91) pp 991-995

[Article by N.A. Rubtsova and R.F. Khayrutdinov, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 541.182.021;549.3;535.372]

[Abstract] *Q*-particles are particles ranging in size from 10 to 10<sup>3</sup> angstroms that have a quantum dimensional effect. CdS, MnO, MoS<sub>2</sub>, and ZnO *Q*-particles are already known to exist. The absorption and luminescence excitation spectra of MoS<sub>2</sub> *Q*-particles have been studied. The MoS<sub>2</sub> particles studied were produced from chemically pure MoS<sub>2</sub> dispersed in argon-saturated pure acetonitrile. The particles' absorption spectra were measured on a Specord UV-VIS spectrophotometer, and their luminescence spectra were measured on a Hitachi-850 fluorimeter. The energies of the optical transitions of the colloidal MoS<sub>2</sub> *Q*-particles synthesized were refined by analyzing the luminescence and luminescence excitation spectra of colloidal solutions of the particles. The following individual bands were identified: 265, 274, 300, 315, 327, 355, 380, and 400 nm. Further analysis established that the optical spectra of the MoS<sub>2</sub> particles studied could be described satisfactorily within the framework of a simple model of a particle in a potential well. The method used to produce the colloidal particles studied was found to yield small plate-like particles with discrete dimensions. Figures 3, table 1; references 15: 13 Russian, 2 Western.

#### **Phase Composition, Structure, and Superconductive Properties of Fluorinated Yttrium-Barium Cuprate**

927M0255A Moscow *NEORGANICHESKIYE MATERIALY* in Russian Vol 28 No 7, Jul 92 (manuscript received 8 Aug 91) pp 1426-1430

[Article by G.M. Kaleva, S.G. Prutchenko, T.A. Starostina, B.Sh. Galyamov, and Ye.D. Politova, Physical Chemistry Scientific Research Institute imeni L.Ya. Karpov; UDC 666.3]

[Abstract] Fluorine-doped specimens of the ceramic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> were subjected to a series of studies to determine their morphology, phase composition, structure, and electrophysical characteristics. The study specimens were produced by solid-phase synthesis involving double annealing from pure Y<sub>2</sub>O<sub>3</sub>, analysis-grade CuO, and analysis-grade BaCO<sub>3</sub> in the following temperature regimens: T<sub>1</sub> = 1,173 K (τ = 20 to 30 hours) and T<sub>2</sub> = 1,208 to 1,223 K (τ = 70 hours). During sintering, the specimens were cooled at a rate of 80 K/h and then held at 623 K for 10 hours or else cooled while still inside the furnace. The fluorine was added by replacing a portion of the barium carbonate in the starting mixture with barium trifluoroacetate, i.e., YBa<sub>2-x</sub>[Ba(CF<sub>3</sub>COO)<sub>2</sub>]<sub>x</sub>Cu<sub>3</sub>O<sub>y</sub> (0 < x ≤ 0.5). By using barium trifluoroacetate in combination with BaCO<sub>3</sub>, the researchers were able to circumvent the problems associated with using gasiform fluorine-containing preparations or reagents containing elements not included in the 1-2-3 phase. Thermooxidative destruction of the barium trifluoroacetate in the temperature interval from 538 to 548 resulted in the formation of BaF<sub>2</sub>. The gaseous volatile decomposition products contained CF<sub>3</sub>COF, COF<sub>2</sub>, and (CF<sub>3</sub>CO)<sub>2</sub>O. X-ray phase analysis of the specimens using a DRON-3M diffractometer established that specimens with x = 0 to 0.09 are virtually single-phase specimens. When x ≥ 0.10, BaF<sub>2</sub>, BaCO<sub>3</sub>, Y<sub>2</sub>BaCuO<sub>3</sub>, BaCuO<sub>2</sub>, and CuO were present along with the 1-2-3 phase. The amounts in which each was present increased as x increased. The parameters a, b, and c remained virtually unchanged in the interval 0 < x < 0.1, the individual crystallites grow, and the edges of the grains are "fused." The findings of electron microscope studies of the local composition of individual grains of a specimen with x = 0.15 using a JSM-35CF microscope were consistent with those of the x-ray phase analysis. The dependences R(T) were measured by the conventional four-probe method in a direct current. When x ≤ 0.10, the change in the specimens' superconductive characteristics corresponded to the change in crystallographic parameters. The "neutral grounding" of R(T) when T [K] 105 K in the case of heterophase specimens with x = 0.15 was particularly surprising, as was the smooth nature of the transition to a state of superconductivity. Figures 4; references 16: 2 Russian, 14 Western.



**Organosilicon and Organophosphorus Compounds With Pseudohalogen Groups. Part 3. Reaction of Alkoxydimethylsilylcyanides With p(IV) Halides**

927M0185F Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 1, Jan 92 (manuscript received 26 Dec 90) pp 187-191

[Article by A.A. Krolevets, V.V. Antipova, P.V. Petrovskiy and I.V. Martynov, Institute of Physiologically Active Substances, USSR Academy of Sciences, Chernogolovka; UDC 547.419.1:547.419.5]

[Abstract] Ongoing studies on the reactivities of alkoxydimethylsilylcyanides involved analysis of their reactions with a series of P(IV) chlorides and fluorides. The essential reaction mechanisms consisted of replacement of two halogen atoms on P(IV) by functional groups ( $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ). Subsequent conversion of the cyanide products to fluorides was attained by reaction with either  $\text{ZnF}_2$  or  $\text{SbF}_3$ . Tables 2; references 17: 11 Russian, 6 Western.

**Organosilicon and Organophosphorus Compounds With Pseudohalogen Groups. Part 4. Synthesis and Properties of Alkoxydimethylsilylisothiocyanates**

927M0185G Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 1, Jan 92 (manuscript received 26 Dec 90) pp 192-196

[Article by A.A. Krolevets, P.S. Dolodov, V.V. Antipova and I.B. Martynov, Institute of Physiologically Active Substances, USSR Academy of Sciences, Chernogolovka; UDC 547.419.1:547.419.5]

[Abstract] Cursory details are presented on the synthesis of alkoxydimethylsilylisothiocyanates in yields of 15-20% by reaction of alkoxydimethylsilchlorosilanes with potassium thiocyanate at 20° C in acetone. Use of ammonium thiocyanate improved the yields to 60-80%. The alkoxydimethylsilylisothiocyanates failed to react with  $\text{SbF}_3$ , but reacted with  $\text{ZnF}_2$  to give methoxydimethylfluorosilane and dimethylfluorosilylcyanide. Reaction with acetyl chloride yielded ethyl chloride and acetoxymethylsilylisothiocyanate. Tables 2; references 15: 7 Russian, 8 Western.



**Synthesis, Properties, and Use of Hydrophilic Polymers and Copolymers of Methacrylic Acid Hydroxyalkyl Ethers**927M0221B Moscow USPEKHI KHIMII in Russian  
Vol 61 No 5, May 92 pp 1002-1019

[Article by Z. G. Asadov, and V. S. Aliyev, Institute of Petrochemical Processes, Azerbaijan Institute of Sciences; UDC 541.64]

[Abstract] The scientific and patent literature on the synthesis of acrylic acid and methacrylic acid hydroxyalkyl ethers from the acids and alkylene oxides, and on polymerization, copolymerization, chemical modification, and properties was reviewed. Various catalysts have been used for these syntheses, including organic trivalent iron compounds, inorganic ferric salts with inorganic promoters,  $\text{AlCl}_3$ , and trivalent chromium compounds. Hydroxyalkyl-(meth)acrylates are obtained with lithium, titanium, zinc, and vanadium additives, and in the presence of organic bases. Water-soluble polymers of 2-hydroxyethylmethacrylate (2HOEMA) are obtained by extraction of dimethacrylates with organic solvents, by conducting polymerization in dilute organic solutions. Irradiation of frozen monomer in a mixture of water and hydrophobic solvent produces high molecular weight polymers. Addition of the cross linking agent ethylene glycol dimethacrylate can produce soluble or insoluble polymers, depending on the level used. Studies have been conducted on the radical polymerization of 2HOEMA, the conformation and hydration of poly-2HOEMA, the kinetics of the polymerization reaction, solvent and temperature effects, and initiator activity. The properties of various copolymers of 2HOEMA and the kinetics of their copolymerization reactions have been investigated. Acrylic acid and methacrylic acid hydroxyalkyl ethers have been found to be highly active in many polymerization reactions, including the formation of graft polymers. Reactions at the OH group of 2HOEMA polymers have been accomplished with alkaline metals, acids, anhydrides, thionyl chloride, phosgene, diisocyanates, and epichlorhydrins. The complex ether groups of 2HOEMA polymers are rather resistant to hydrolysis, permitting directed hydrolysis of copolymers. Reactions of 2HOEMA with amines, hydrazines, silico-organic compounds, and dianhydride complexes. Halogen derivatives of 2HOEMA polymers have been reacted with oxazolines, followed by sodium imidazole, to form polymers containing the imidazole ring. Copolymers of 2HOEMA are used in contact lenses, hydrogel carriers for biologicals and pharmaceuticals, implants, microencapsulation media, coatings, and adhesives. References 158: 48 Russian, 1 Slovak, 109 Western.

**Thin-Layer Photochemical Copolymerization of Ethylene Glycol Dimethacrylate-N-Toluylenecarbamate**927M0247E Ivanovo IZVESTIYA VYSSHIKH  
UCHEBNYKH ZAVEDENIY: KHIMIYA I  
KHIMICHESKAYA TEKHOLOGIYA in Russian  
Vol 35 No 4, Apr 92 (manuscript received 24 Sep 91)  
pp 98-102

[Article by L.A. Onosova, L.P. Butba, and G.M. Tseytlin, Department of the Chemistry and Technology of Polymer Film-Forming Materials, Moscow Chemical Technology Institute imeni D.I. Mendeleyev; UDC 678.7:678.664]

[Abstract] The process of thin-layer photochemical copolymerization was studied by way of the example of the photochemical copolymerization of ethylene glycol dimethacrylate-N-toluylenecarbamate [EDMTC] from the comonomers butylmethacrylate, glycidyl methacrylate, and triethylene glycol (TGM-3). The copolymerization process was conducted in films measuring  $40 \pm 5$   $\mu\text{m}$  in thickness that were formed directly on glass substrates in air. A DRT-1000 mercury lamp served as the UV radiation source, and isopropyl benzoate was used as a photoinitiator. The optimal concentrations of active comonomers, i.e., the concentrations at which the initial polymerization rate was at a maximum, in the different compositions were determined as follows: butylmethacrylate, 10-15; glycidylmethacrylate, 81-23; and TGM-3, 20-30. The copolymerization constants of each of the three pairs of comonomers were also found: for EDMTC-butylmethacrylate,  $r_1 = 2.26$  and  $r_2 = 0.26$ ; for EDMTC-glycidylmethacrylate,  $r_1 = 0.56$  and  $r_2 = 0.26$ ; and for EDMTC-TGM-3,  $r_1 = 1.38$  and  $r_2 = 0.4$ . Of the three copolymerized systems studied, only EDMTC-glycidylmethacrylate had a copolymerization constant of less than 1, which confirms the presence of an azeotropic composition in the said system (EDMTC:glycidylmethacrylate = 43:57%). Figures 4, table 1; references 6: 3 Russian, 2 Western.

**Hydrophilicity of the Surface of Powders of Copolymers of Methyl Methacrylate and Methacrylic Acid**927M0248C Ivanovo IZVESTIYA VYSSHIKH  
UCHEBNYKH ZAVEDENIY: KHIMIYA I  
KHIMICHESKAYA TEKHOLOGIYA in Russian  
Vol 35 No 2, Feb 92 (manuscript received 21 Jun 91)  
pp 67-70

[Article by Ye.V. Borisov, M.A. Lagutin, O.I. Vlaskina, and Yu.L. Shishkin, Organic Chemistry Department, Moscow Pedagogical State University imeni V.I. Lenin; UDC 541.64:547(39+412.2)]

[Abstract] The methods of thermogravimetry, differential thermal analysis [DTA], and x-ray photoelectron spectroscopy were used to determine the hydrophilicity of the surface of powders made of copolymers of methyl methacrylate and methacrylic acid (with the amounts of

the latter ranging from 5.2 to 20.2%). The studies were performed on a Q-1500D thermal analyzer, MKAT-1 microcalorimeter, and a Rebier SIA-200 spectrometer. The thermogravimetry and DTA curves established that the stage of dehydration of polymethyl methacrylate from the powder's surface is very weakly expressed. Thermal destruction begins at temperatures above 250° C and, in an inert atmosphere, culminates in the total vaporization of methyl methacrylate at 430° C. When copolymers containing about 10% methacrylic acid are heated above 40° C in air or in an inert atmosphere, there is a primary mass loss amounting to about 2% of the powder's total mass. The process of thermal destruction begins above 210° C in air or 250° C in an inert atmosphere. This process includes three stages that are well demarcated under quasi-isothermal conditions (a specimen decomposition rate of 1 mg/min). Above 300° C a complex depolymerization process occurs that results in the formation of methyl methacrylate, carbon oxides, and methane. The mass loss of specimens containing 20.2% methacrylic acid that are heated to 355° amounts to about 15%. Above that temperature, thermal destruction increases sharply, culminating in the total decomposition of the specimen at 480° C. The studies confirmed that there is a link between the content of carboxyl groups and water on the one hand and the chemical composition of the polymer chains on the other hand. Figures 2; references 9: 6 Russian, 3 Western.

#### The Calculation of Polymers' Wetting Contact Angle

927M0248D Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 35 No 2, Feb 92 (manuscript received 7 May 91) pp 71-74

[Article by L.N. Mizerovskiy, Institute of the Chemistry of Anhydrous Solutions, USSR Academy of Sciences; UDC 678.049.7:539.193]

[Abstract] The existing literature data on the wetting contact angles ( $\theta$ ) of a number of polymers (polytetrafluoroethylene, polytrifluoroethylene, polyvinylidene fluoride, polyethylene, polyvinyl fluoride, polyvinylidene chloride, polyvinyl chloride, polyhexamethylenedipamide, polystyrene, and polyethyleneterephthalate) were subjected to a statistical analysis. The analysis demonstrated that for fluids that do not spread out with respect to the polymer (i.e., those fluids whose specific surface free energy is greater than their critical surface wetting tension),  $\cos \theta$  is an unequivocal function of two characteristic parameters of the latter, i.e., critical surface wetting tension  $\sigma_{cr}$  and critical nonwetting tension  $\sigma_{cr}^*$ , as well as the fluid's surface tension  $\sigma_L$ . Refined values of  $\sigma_{cr}$  and  $\sigma_{cr}^*$  for the 10 polymers mentioned above are presented. Figure 1, table 1; references 9: 7 Russian, 2 Western.

#### Chemical Methods of Treating the Surface of Inorganic Nonmetal Materials

927M0249A Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 35 No 3, Mar 92 (manuscript received 16 Jul 91) pp 15-22

[Article by E.G. Rakov, Rare and Disperse Elements Technology Department, Moscow Chemical Technology Institute imeni D.I. Mendeleev]

[Abstract] Chemical methods of treating the surfaces of blanks and finished products made of inorganic materials may be divided into techniques based on chemical etching and chemical deposition of coatings. Chemical etching is widely used in electronics and related fields. It offers several important advantages over machining (cutting, drilling, milling, grinding, polishing, etc.). Specifically, chemical etching makes it possible to manufacture products with much more complicated configurations than is otherwise possible, reduce the sizes of such components to micron or submicron size, increase the quality of surface treatment and hence the performance characteristics of instruments, reduce the consumption of scarce materials, and increase labor productivity. Four main approaches to chemical etching are currently in use. Chemicomechanical etching involves both chemical and mechanical processes and exists in several different versions, including the use of a chemical reagent capable of reacting with a material as it is machined by a disk or abrasive filament, the use of an abrasive suspension in a fluid that is chemically reactive with respect to the material being machined, and the use of colloidal particles containing an active chemical reagent. The second chemical etching method, i.e., chemical etching in solutions, may be used with a variety of materials including quartz, piezoelectrics, semiconductors, glass, and granular materials. The third chemical etching method, i.e., etching in melts, has been developed to overcome the shortcomings and limitations of using aqueous solutions to modify surfaces; fluoride melts appear particularly promising. Gas etching, the fourth main chemical etching technique, may be used to strengthen materials with a very complex composition (e.g., glass) and is generally performed with HF. Chemical precipitation of coatings from the gaseous phase (especially activated chemical precipitation from the gaseous phase) is perhaps the most important chemical surface treatment method, and the production of diamond films is one of its most important applications. References 54: 51 Russian, 3 Western.

#### Kinetics of Combined Milling of Polymer Materials in a Roller Grinder

927M0249B Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 35 No 3, Mar 92 (manuscript received 15 Mar 91) pp 89-94

[Article by T.N. Nesiolovskaya, Ye.M. Solovyev, V.A. Yazev, and S.M. Durosov, Chemical Technology of

Elastomer Processing Department, Yaroslavl Polytechnic Institute; UDC 678.023.053]

[Abstract] A study examined the laws governing the combined grinding of two polymer materials with fundamentally different structures, i.e., rubber crumbs and cordage fiber, in an effort to develop effective regimens for processing them. The efficiency of a combined grinding process was evaluated from the standpoints of the kinetic and energy coefficients of grinding, which reflect the intensity of grinding and the efficiency of the energy expended on the process, respectively. The ratio of the components of the polymer composite and the characteristics of the fiber involved (specifically, the fiber's length and the presence of a finish on the fiber's surface) were both shown to effect grinding process efficiency. Finishing the fiber made it possible to increase the intensity of the grinding process (thanks to an increase in the friction coefficient of the finished fiber along the roller surface) but resulted in a decrease in the energy coefficient (probably because finished fiber is stronger than unfinished fiber and thus requires more energy to grind). The starting characteristics of the fiber had a greater effect on grinding process efficiency than did any of the parameters of the process of grinding on roller equipment (e.g., the gap between the rollers). The starting characteristics of the fiber also affected the dependence of the energy and kinetic coefficients on the ratio of components in the polymer composite undergoing grinding. Tables 2; references 7 (Russian).

#### **Producing a Homogeneous Copolymer in a Semi-Intermittent Reactor Under Conditions of Heterophase**

927M0249C Ivanovo IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 35 No 3, Mar 92 (manuscript received 16 Jul 91) pp 100-103

[Article by V.L. Perov, V.P. Belkov, and A.T. Abduvaliyev, Department of Flexible Manufacturing Systems, Moscow Chemical Technology Institute imeni D.I. Mendeleev; UDC 66.011.001.57.075:66.048]

[Abstract] A heterophase process of radical copolymerization has been proposed for use as a model for use in the commercial-scale production of a homogeneous copolymer (such as a prolonged-action plant growth regulator) in a solution in a semi-intermittent reactor. The model is based on the experimentally established fact that sorption factors have only a negligible effect on the compositions of the reaction medium in different phases, as well as on the following assumptions for a biphasic model: the ratio of the polymerization rates in the two phases is constant, the kinetic constants do not change with the conversion, the compositions of the reaction mixture in both phases are constant, and the content of polymer in the solid phase is negligible. The series of 16 equations presented make it possible to determine the optimum rate of feeding the more active

of the two comonomers into the reactor so as to prevent a shift in the copolymer's composition during the course of the conversion process. The model may be used to determine the degree of the monomers' conversion at any moment in time. Continuous feeding of the more active of the two comonomers in accordance with the proposed model boosts process efficiency by facilitating an increase in the yield of end product. References 9: 6 Russian, 3 Western.

#### **Basic Laws of the Sorption of Water by Polymeric Materials**

927M0253A Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 66 No 7, Jul 92 (manuscript received 20 Jun 88) pp 1713-1735

[Article by A.I. Gantman, Chemistry Institute, Far Eastern Department, Russian Academy of Sciences, Vladivostok; UDC 541.183]

[Abstract] Like other ion-containing polymers, polymeric ion exchangers, which are widely used both in industry and power generation, absorb water well, changing their properties in the process. The absorption of water by ion exchangers results in the dissociation of ionogenic groups and the formation of mobile ions that in turn further intensify water absorption. After analyzing the experimental data available in the existing Western and Russian literature on the topic, the author of this review has developed a mathematical model of the basic laws governing water sorption by polymeric materials. The model includes consideration for the following: the structural model of an ion exchanger; water sorption by a dry ion exchanger; water absorption and nonexchange sorption of electrolytes; and the dependence of water absorption on ionic composition, temperature, and pressure. The proposed model is said to also be suitable for describing the sorption of water by bifunctional ion exchangers, for example, by highly basic anion exchangers containing weakly basic groups. Figures 11, tables 3; references 97: 66 Russian, 31 Western.

#### **Polymeric Coatings Based on Polyethylene With Reduced Gas Permeability**

937M0009A Moscow DOKLADY AKADEMII NAUK in Russian No 1, Jan-Feb 92 pp 16-17

[Article by N.I. Mashukov, O.A. Vasnetsova, A.Kh. Malamatov, and G.V. Kozlov, Kabardino-Balakarskiy State University Nalchik, and MMA [not further identified] imeni I.M. Sechenov, Moscow; UDC 541.64:536:537.1'128+678.048]

[Abstract] It has been shown previously that adding a highly dispersed mixture of Fe and FeO to high-permeability polyethylene reduces its coefficient of gas permeability with respect to nitrogen [ $P_{N_2}$ ]. Analogous results were achieved by adding small amounts (up to 5



wt.-%) epoxy polymer [EP] to high-permeability polyethylene [HPPE]. The resultant polymeric materials possessed high thermal oxidation stability and chemical resistance to corrosive media. These properties may be explained within the framework of the theory of fluctuation free exchange and the cluster concept of the structure of polymers. The dependences of the natural log of the nitrogen permeability coefficient on the volume fraction of fluctuation free exchange ( $f$ ) for the two composites HPPE + Fe + FeO and HPPE + EP yield a similar correlation for both composites that confirms the expected increase in gas permeability as  $f$  increases. The experimentally observed approximately 15-fold decrease in  $P_{N_2}$  for the composite HPPE + 0.05(Fe + FeO) as compared with that of starting HPPE may be explained within the framework of the cluster concept of the structure of the amorphous state of polymers, which assumes the presence of clusters consisting of densely packed collinear segments surrounded by a loosely packed matrix so that diffusion processes occur in the loosely packed matrix where the entire fluctuation free exchange is concentrated. A series of equations is presented to explain the behavior of HPPE + Fe + FeO and HPPE + EP within the framework of these theories. Figure 1; references 10: 5 Russian, 5 Western.

#### **Polymer Building Materials and Equipment To Process Them**

937M0011E Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 p 46

[Article by V.A. Novak, S.M. Andreyeva, N.G. Kirichenko, O.Yu. Krasnova; UDC 678.027:69]

[Abstract] The use of polymer building materials has made it possible to reduce the mass of enclosing structures by a factor of 5 to 10; reduce the labor input required for construction operations by a factor of 2 to 3; free up scarce metal, cement, and wood; and cut down on fuel consumption. The USSR construction industry uses about 500,000 tons of polymeric materials annually (about 10% of the entire amount produced). Of that amount, 100,000 tons consists of foamed plastic based on polystyrene, polyurethane, and phenol-formaldehyde resins. More than 80% of these foamed plastics are produced on site by pouring a three-component composition directly into molds of different sizes and shapes or by pouring a mixture of components directly onto the panel joints being insulated. About 20% of the foamed plastics are used in two- or three-layer sandwich panels. Most such building materials are currently processed in domestic spraying equipment (such as the PENA 9) and imported equipment produced by the firms Plasttechnik Greiz GmbH and Ernst (Germany), Metekno and Fata (Italy), and Sekmer (France). Most of the equipment used is imported from Plasttechnik Greiz GmbH. One especially important piece of equipment manufactured by Plasttechnik Greiz GmbH is a low-pressure unit for producing shaped products from foamed polystyrene. The unit is available in three models that are capable of producing products measuring 640 x 400 x 350, 850 x

680 x 320, and 800 x 1,250 x 400 mm, respectively. The different models require 2.2, 1.5, and 5.5 kW of power, respectively. The units can also be used to produce hollow foamed polystyrene blocks measuring 120 x 25 x 25 cm that may be used to erect the walls of one-story buildings. After being laid, the blocks are filled with a concrete solution. Such homes may be built in a week from no more than 200 blocks weighing 1 kg each. Table 1.

#### **Combined Technology for Production of Composite Polymer Materials in a Continuous Process**

937M0019A Moscow PLASTICHESKIYE MASSY  
in Russian No 4 Apr 92 p 5

[Article by A. N. Imanov, I. G. Musalimov, T. A. Bespalova, Yu. M. Budnitskiy, N. V. Ganiyeva; UDC 678.5.033.02]

[Abstract] An attempt was made to develop a continuous method for production of composite polymer materials using a continuous milling process for the fillers, activation of their surface and combination with powdery polymer. The milling was performed in a stream setting with an adapter for removal of static electricity. The milled material was sorted out by the particle size, the proper size batch was mixed with polymer powder and the modifier, it was then homogenized and granulated. Comparison of the end product obtained by this stream-vortex method with the material obtained by the traditional or by the activation method showed the former to yield the strongest material at the lowest cost. Table 1; figure 1.

#### **Use of Waste Products From Manufacture of Acetate Fiber for Production of Layered Plastics Based on Etrol**

937M0019B Moscow PLASTICHESKIYE MASSY  
in Russian No 4 Apr 92 pp 24-25

[Article by A. Sh. Sharipdzhanov, I. M. Abdiraimov, M. M. Gulyamova; UDC 678.544.4:677.014]

[Abstract] Ether-cellulose plastics can be used as decorative sheets in manufacturing of furniture, in automobile industry or in finishing home appliances. Due to shortages of the starting materials, domestic production of such plastics is below the demand level. Therefore, an attempt was made to evaluate the use of waste products from manufacturing acetate fibers as possible starting material for layered plastic. Spent filter cloth (SFC) were used as reinforcing fillers and binders; primary and secondary acetyl cellulose etrol was also used as a binder. Analysis of the data obtained on the finished product showed that material with 20% SFC lowered its hardness in comparison to kaoline containing etrol from 1.5 to 0.8 g/cm<sup>3</sup>, but provided higher shock viscosity (from 15 to 40 kJ/m<sup>2</sup>). The optimal quantity of SFC was shown to be about 10-15% (based on etrol). Overall, an estimate was

made that using the SFC in this process should result in a 20% saving of the starting material and in the general preservation of clean environment. Tables 2; figures 2; references: 8 (Russian).

**Modification of Polymer Film Materials and Prediction of Changes in Their Operational Properties With Consideration of Aging Processes**

937M0019C Moscow PLASTICHESKIYE MASSY  
in Russian No 4 Apr 92 pp 26-28

[Article by G. Sh. Keydiya, M. G. Alaniya, K. S. Isayev, F. B. Tynysbayev, Yu. V. Zelenev]

[Abstract] To improve the properties of polymer films, they are modified with fluorine containing elastomers; this increases their elasticity, thermal stability, wear resistance and resistance to aggressive media. Because of the fact that all physical properties depend on their molecular mobility, the relaxation phenomena of polymer films were investigated in a wide range of temperatures. In this paper the authors reviewed the work of the aging of Laysan films as it related to structural characteristics, the surface layer properties, chemical modifications, physical modifications (thermal, electric, optical), etc. A formula was reproduced which could be used to calculate the aging rate of polymer films. It was noted that during the aging process, molecular weight of the polymer was decreased along with the formation of cross-linking bonds, double bonds and with accumulation of carbonyl groups resulting from oxidative processes. Table 1; references: 10 (Russian).

**Effect of Polymer Films Modification by Single and Dual Axis Drawing on Their Molecular Mobility**

937M0019D Moscow PLASTICHESKIYE MASSY  
in Russian No 4 Apr 92 pp 38-39

[Article by Yu. V. Zelenev, M. G. Alaniya, G. Sh. Keydiya]

[Abstract] Single and dual axis drawing of polyvinyl chloride and polytetrafluoromethyl film was investigated primarily at room temperature with only some runs

performed at about 50° C above the vitrification temperature. Local and segmental forms of molecular mobility were noted in a wide range of temperatures and frequencies evaluated. In case of single axis oriented PVC films, the dielectric loss angle vs. temperature graph showed two maxima: a low temperature (20-50° C) and a high temperature (115- 145° C) one corresponding to local and segmental processes respectively. In comparison to the starting film, this represents a shift towards higher temperatures. The dual axis oriented films show no such shift. Figures 2; references: 6 (Russian).

**Product Deformation Dynamics in Processes of Pneumo-Formation of Hollow Polymer Articles**

937M0019E Moscow PLASTICHESKIYE MASSY  
in Russian No 4 Apr 92 pp 40-43

[Article by B. V. Berdyshev]

[Abstract] An attempt was made to develop a mathematical model describing the deformation dynamics of various products during the pneumo-formation of hollow polymer articles. In general, there are many parameters affecting this process: rheological properties of the material used, thermodynamic parameters of the gas within the hollow volume of the article being produced, etc. The model was designed to cover all variables. Several assumptions had to be made: the adiabatic gas flow was considered critical; the gas reservoirs had infinite capacity (i.e. their volume was at least one order of magnitude greater than that of the article being formed); there was no heat exchange between the gas and the product; the complex process of gas flow into the article being formed was handled as two consecutive processes: simultaneous adiabatic change of the gas entering and the gas present in the hollow followed by instantaneous isobaric temperature equilibration of both components. Data obtained from the model agreed adequately with experimental values; the 20% difference was most probably due to the simplification assumptions made. Figures 2; references 7: 6 Russian, 1 Western.



**Radiation Chemistry of Crown Compounds**

927M0221A Moscow USPEKHI KHIMII in Russian  
Vol 61 No 5, May 92 pp 883-909

[Article by V. V. Makhlyarchuk, and S. V. Zamonskiy,  
Moscow State University imeni M. V. Lomonsov,  
Chemistry Department; UDC 541.15:547.898]

[Abstract] The radiochemistry of crown ethers and their analogues was reviewed and analyzed. One of the most important aspects of crown compound radiochemistry is their use as extracting agents for radionuclide anions. Methods have been reported for the extraction of uranium, neptunium, thorium, plutonium, technetium, astatine-211, iodine-131, radium, cesium-137, and strontium-90 from solids (such as spent fuel) and acidic aqueous solutions containing various other components. In many cases certain crown compounds show high selectivity for one or more important radionuclide, sometimes accompanied by increased stability to  $\gamma$ -radiation. Radiolytic decomposition of solvents such as chloroform and of membranes must also be considered. Several investigators have identified products of crown ether radiolysis. Mechanisms involve an initial carbon radical, peroxidation, ring cleavage, reaction with solvent and acid, and subsequent fragmentation. Ion pair reagents and immobilized liquid membranes and sorbents have been used to improve crown ether extraction

of cesium and strontium. The advantages of using non-chlorinated organic solvents for crown ether extractions of radionuclides have recently been demonstrated. Studies on the mechanism of radiolysis have included detection of solvated electrons using pulse radiolysis, and of radical intermediates using low temperature  $\gamma$ -radiation and EPR, including spin trap methods. Factors affecting crown ether stability under irradiation have been measured, and GC and mass spectroscopy have been used to study radiolysis products. Crown ethers were found to have similar radiochemistry to dioxane and polyethylene glycols. Impulse radiolysis has demonstrated that crown ethers in water react easily with atomic hydrogen and OH and O $\cdot$  radicals, resulting in crown ether dehydration to the same radical in all three cases with subsequent dimerization or recombination. Similar studies were conducted with crown ether metal ion complexes and nitrogen analogues of crown ethers. Several mechanisms have been proposed for the formation of aldehydes when aqueous solutions of crown ethers are exposed to high doses of radiation. The presence of crown ethers was not found to increase the radiation sensitivity of aromatic hydrocarbon solvents. Some protection from dimerization was noted. Crown ethers have been used to solubilize inorganic electron donors in aromatic hydrocarbons, decreasing radiation-induced dimerization. Figures 4; references 142: 65 Russian, 77 Western.

**The Formation Diversity of Gold-Silver Deposits**

927M0250A Moscow DOKLADY AKADEMII NAUK  
SSSR in Russian Vol 323 No 1, Mar 92 (manuscript  
received 15 Jan 92) pp 129-132

[Article by A.A. Sidorov, corresponding member, North-eastern Integrated Scientific Research Institute, Far Eastern Department, Russian Academy of Sciences, Magadan; UDC 553.41:551.31]

[Abstract] A recent analysis of a group of gold-silver deposits has made it possible to view them as members of genetically diverse ore formation series. In the past, the similarity of the physicochemical conditions under which the ores were deposited has often caused researchers to erroneously confuse this similarity of conditions of deposition with genetic similarity. It is the contention of the authors of the analysis reported herein, however, that the base ore formations analyzed may be separated into the following series of gold-silver ore formations: copper-porphyric, tin (silver)-porphyric, gold-sulfide, pyrite, as well as five-element formations and copper-nickel and chromite. The gold-silver deposits in these genetically diverse series, which have been named on the basis of their basic formation, all have very different outward appearances. The copper-porphyric series is essentially the classic gold-silver deposit that has been studied long and well, especially within the confines of volcanogenic provinces; one example is the San Juan region in Colorado. The deposits of the copper-nickel and chromite series characteristically containing gold-silver-telluride deposits formed in which the gold-silver deposits have an epigenetic relationship to the rest of the deposit (as in the Zodskeye deposit in Armenia and the Aginskoye deposit in Kamchatka). The tin (silver)-porphyric deposits are orogenic. The gold-silver deposits in such base formations represent the initial and final (high- and middle-temperature) elements of the series and exist in the Omsukchan region and in northeastern Russia. The gold-sulfide members of the series may also be classified as orogenic and the final (low-temperature) elements of the series. The exist in the Chukotskiy region and in northeastern Russia. The geological conditions of the development of the pyrite deposits include geosynclinal, submarine, and early orogenic. The gold-silver deposits in this series of deposits bear an epigenetic (medium- and low-temperature) relationship to the base formations and are found in Japan. The five-element formations are of subplatform and reef origin. The gold-silver deposits in these formations also bear an epigenetic relationship to the base formations. Such formations are found in southern Australia and central Europe. Table 1; references 8 (Russian).

**Diamond Surface Radicals in Thermal Desorption, Chemisorption, and Gasification Reactions**

927M0252E Moscow KHIMICHESKAYA FIZIKA  
in Russian Vol 11 No 7, Jul 92 (manuscript received  
11 Sep 90) pp 1002-1007

[Article by A.M. Abyzov, S.L. Panasyuk, B.Ya. Zorin, and Ye.P. Smirnov, Leningrad Technological Institute imeni Lensovet; UDC 541.183:546.26:543.422.27]

[Abstract] The formation of diamond surface radicals during thermal desorption, chemisorption, and gasification reactions were studied in a vacuum and in a flowthrough inert gas atmosphere. AM-3 natural diamond powder (specific surface, 12 m<sup>2</sup>/g) was used. The technique of liquid-phase oxidation (boiling in perchloric acid for 2 hours, rinsing in water, and air-drying at 100° C) was used to saturate the surface of the starting preparation with oxy groups in a concentration of about 25 μmol per m<sup>2</sup> adsorbed oxygen atoms. The starting preparations were then subjected to thermal desorption in a vacuum or a combination of thermal desorption and reaction with O<sub>2</sub> and N<sub>2</sub>O in an inert medium. The ESR spectra of the starting and processed specimens were recorded and compared. Stable diamond surface radicals were shown to form during thermal desorption. The thermal desorption mechanism of the formation of stable surface radicals could not be verified with carbon-graphite materials. This difference between the behavior of diamond and carbon-graphite materials was echoed in the experiments involving chemisorption and gasification in a pulsed mode: In the case of the diamond powder, the reaction rate was linearly dependent (in the case of N<sub>2</sub>O) on the degree of transformation of the solid phase with a high degree of nonstationarity. In the case of the graphite, on the other hand, the said dependence was exponential with weak nonstationarity. Figures 4, table 1; references 16: 13 Russian, 3 Western.

**Morphology of the Set Sign 100 Facet of a Synthetic Diamond Single Crystal**

937M0003A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 134 No 5, Jun 92 (manuscript received  
26 Mar 92) pp 1031-1033

[Article by V. G. Balakirev and V. A. Laptev (All-Union Synthetic Mineral Research Institute, Aleksandrov Vlademirskaya Oblast, presented by Academician Yu. A. Buslayev, 6 Mar 92; UDC 621.921.34:666.333]

[Abstract] Parallel lines on the surface of the set sign 100 facet of a synthetic diamond are not scratches on the crystal surface but constitute scratches on the replica itself. These scratches are formed by the action of very hard particles, believed to be titanium and perhaps other carbide crystals (0.05-0.2 μ) during the replica isolation process. In addition, pits (> 1 μ) with fine particles and "empty" pits are observed. The pits are two-tiered: the first are pyramid-shaped with square bases, and the second is flat-bottomed and has bases which are in the shaped of a square, an isosceles trapezoid, or an equilateral triangle. A preliminary explanation of the unusual morphology is offered. References: 4: 3 Russian, 1 Western.

**Facies of the Depth of Deposits of an Inversive Pluton- Bearing Gold Quartz Formation of Southern Kazakhstan**

937M0003B Moscow DOKLADY AKADEMII NAUK in Russian Vol 134 No 5, Jun 92 (manuscript received 2 Apr 92) pp 1076-1080

[Article by E. M. Spiridonov, Moscow State University imeni M. V. Lomonosov, presented by Academician A. A. Marakushev 2 Apr 92; UDC 553.411+549.283(574.2)]

[Abstract] Minerals associated with gold deposits in Southern Kazakhstan are reported at depths up to 12 km. As the depth increases, the amount of Sb, Hg, and Tl decreases, and the amount of Te, W, and Au/Ag increases. The value of Te/Se increases from 1-2 to 100-3000, and the value of Au/Hg increases from 200-8500. The fixation of Sb, Hg, Tl, and Se predominantly at a depth up to 3 km is probably due to their high volatility. Te (tellurides) are at greater depths because the dissociation temperature of H<sub>2</sub>Te is higher than that of H<sub>2</sub>S. The deposits were formed under relatively ordered conditions, and this explains the stable composition of the ores and ore minerals along the verticals of specific deposits and the differentiation of facies at different depths. References: 15: 14 Russian, 1 Western.

**Thermodynamics of Perchlorate Compounds of Silver in Aqueous Solutions**

937M0014A Dushanbe DOKLADY AKADEMII NAUK TADZHIKSKOY SSR in Russian Vol 34 No 7, Jul 91 (manuscript received 28 Feb 91) pp 431-434

[Article by V. S. Chekushin, Ye. I. Pavlova, Ye. V. Chekushina, correspondent member AS Tadjikskoy SSR P. M. Solozhenkin, Krasnoyarsk Institute of Non-ferrous Metals imeni M. I. Kalinin, Institute of Chemistry imeni M. I. Nikitin, AS Tadjikskoy SSR; UDC 541.49]

[Abstract] Composition of silver perchlorate compounds was studied by electrochemical methods and stability constants were determined. Solutions of the compounds were prepared with the use of silver oxide and chemically pure perchloric acid. Discussion of the results included data obtained by potentiometric and potentiostatic

methods on a P 5838 potentiostat with the use of silver and chlorosilver (comparison) electrodes. The studies showed a variability and uncompensativeness of the ionic strength of the solutions studied because of difficulties connected with selection of salts of electrolytes showing unconditional indifference with respect to the silver ions in the aqueous solutions. The perchlorate solutions formed compounds of Ag(ClO<sub>4</sub>) composition, the resistance of which is determined by the value  $[b<]_{\infty}=17.7 + \text{or} - 1$ . Figures 2; references 5 (Russian).

**Formational Diversities of Gold-Silver Deposits**

937M0015A Moscow DOKLADY AKADEMII NAUK in Russian Vol 323 No 1, Mar 92 (manuscript received 15 Jan 92) pp 129-132

[Article by A. A. Sidorov, correspondent member of RAS; North-Eastern Combined Scientific Research Institute; Far Eastern Department of the Russian Academy of Sciences, Magadan; UDC 553.41:551.31]

[Abstract] Analysis of a group of gold-silver deposits by a recently developed method [Sidorov A. A., Ore Formations of Phanerozoic Provinces, Magadan, 1987] showed that these deposits consist of members of genetically different ore formational series. The similarity of the deposits was caused by similar physico-chemical conditions of deposition of the ores which is frequently identified with genetic similarity. The basic ore formations included the following series of gold-silver ore formations: copper-porphyrin, tin (silver)-porphyry, gold-silver, gold-sulfide and pyrite and also 5-element, copper-nickel and chromite formations. Series according to the basic formation, characteristic mineral types of the gold-silver formations, geological conditions of development of the series, relationship of gold-silver deposits to basic formation and examples of each were tabulated and discussed. It was found that gold-silver deposits related to the class of epithermal deposits represent at least 6 ore formations, entering into different formational series. It was assumed that most vein deposits combined in classes and formations according to physico-chemical conditions of deposition of ores also are genetically heterogeneous convergent formations. References 8 (Russian).

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